STUDY OF CRYSTALLIZATION OF GLASS

BY

HOWARD RAYMOND SWIFT

B.S., University of Illinois, 1940

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AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
ENGINEERING IN THE GRADUATE SCHOOL OF
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STUDY OF CRYSTALLIZATION OF GLASS

I. Introduction

If a crystal is placed in a liquid which is supersaturated with respect to this material, the crystal will increase in size. It was the purpose of this investigation to add to the knowledge concerning the factors which influence the rate of growth of such a crystal.

The study was limited to crystal growth measurements in some soda-lime-silica glasses since these glasses are of a rather simple type, are of great commercial interest, and have rates of devitrification sufficiently low so that the crystal development can be readily followed. The data may be of value in reaching a better understanding of the transition from the liquid to the solid state in general.

II. Literature

The work that has been done on crystal growth in glasses may be divided into two divisions: (a) study of phase equilibrium relationships, and (b) measurement of the rates of crystal growth in different glasses.

The work of Morey and Bowen [1-4] is outstanding in regard to the determination of the phase equilibrium relationships which are of interest to the glass technologist. Such data define the upper limit of crystal growth of the various phases in the glasses as well as the solubility of the phases at temperatures below the liquidus.

Dietzel, Zschimmer, and Mullensiefen [5-9] measured the rates of growth of crystals in soda-lime-silica glasses of varying composition by measuring the lengths of crystals formed after exposing the glasses to different temperatures for varying lengths of time.

III. Studies of Rate of Crystal Growth in Glasses

A. *Procedure*

A series of soda-lime-alumina-silica glasses was made with the alumina varying in steps of two percent from zero to eight percent alumina replacing the silica (17% Na_2O; 12% CaO; 0-8% Al_2O_3; 71-63% SiO_2). These glasses were melted in platinum,

ground, and remelted. A similar series with magnesia replacing the lime was obtained from the General Research Laboratory of the Owens-Illinois Glass Company (16% Na_2O; 10-0% CaO; 0-10% MgO; 74% SiO_2). The compositions, liquidus temperature, identity of the primary phase precipitating on crystallization, and viscosity data were published by the above laboratory.[10]

Devitrification tests were conducted by two methods:

Method A. One-quarter inch samples of the glasses were placed on a flat piece of platinum-rhodium foil and heated in a Glo-Bar furnace at various temperatures (from 700°C. to 1000°C.) for varying lengths of time (one to sixty-four hours). A Chromel-Alumel thermocouple was placed near the center of the sample holder.

The devitrified samples were sectioned for crystal length measurements. Devitrification practically always began at the surface with the crystals projecting inward, and the thickness of this devitrified zone was used as a measurement of the maximum crystal length.

Method B. For measurement of the rate of crystal growth near the liquidus temperature and for measurement of the rate of solution of the crystals at temperatures above the liquidus, it was necessary to change the above procedure. Samples of the glass weighing approximately 0.04 grams were placed in a very small platinum-rhodium cup which had a hole in the bottom. The sample holder was so fashioned that it could be attached directly on the end of the thermocouple tube. The platinum-platinum rhodium thermocouple was bent so that the junction was as close as possible to the surface of the sample without touching it.

The glass was heated at approximately fifty degrees above the liquidus temperature in a platinum-wound gradient furnace to enable the sample to assume the shape of the holder. The sample was then moved so that its temperature was approximately thirty degrees below the liquidus temperature and crystals were allowed to form. The sample was removed from the furnace, placed on a microscope stage, and the lengths of the crystals measured using transmitted light. Sketches were made of the crystals so that they could be relocated.

The sample was then placed in the cold end of the furnace, preheated for approximately one-half hour as the furnace was regaining thermal equilibrium, and slid into the hot zone. A Type K Leeds and Northrup potentiometer was used for the temperature measurements. By varying the position of the sample in the furnace and watching the deflections of the galvanometer, the temperature of the thermocouple was maintained within a degree or less of the desired temperature.

After a predetermined length of time, from two to sixty minutes, the sample was quickly removed from the furnace and air-cooled. The crystal lengths were remeasured and the increase or decrease in size noted.

B. *Results*

Devitrite crystals precipitated as the primary phase in the base glass containing no alumina. As the alumina content was increased, the maximum rate of linear growth of devitrite was progressively decreased. The liquidus temperature for devitrite was slightly increased with the addition of alumina.

Wollastonite crystals appeared as the secondary phase in the glass containing four percent alumina. As the alumina was increased, wollastonite became the primary phase. The rate of crystal growth for wollastonite was approximately the same in the glasses with four and six percent alumina but increased as the alumina was raised to eight percent. The temperature at which crystals of wollastonite were in equilibrium with the melt was progressively increased with the replacement of silica with alumina.

The rate of solution vs. temperature curve for devitrite and wollastonite in the glasses with variable alumina content was continuous with the rate of growth vs. temperature curve, if solution is considered to be negative growth. The rate of solution increased very rapidly as the temperature was increased beyond the liquidus.

Cristobalite crystals appeared as the primary phase in the base glass with no magnesia. As magnesia replaced the lime, the liquidus temperature for cristobalite progressively decreased, and the maximum rate of crystal growth decreased very rapidly.

Devitrite crystals appeared as a secondary phase in the glass with no magnesia. With the replacement of lime with magnesia, the temperature at which devitrite was in equilibrium with the melt decreased, and the maximum rate of crystal growth rapidly decreased.

Diopside crystals were present as a secondary phase in the glass with six percent magnesia and as the primary phase in the glass containing eight percent magnesia. The temperature at which diopside was in equilibrium with the melt increased as the magnesia increased; the maximum rate of crystal growth also increased with magnesia.

A sodium magnesium silicate, $Na_2O \cdot 2MgO \cdot 6SiO_2$, appeared as the primary phase in the glass with all of the lime replaced by magnesia. This material had a higher rate of growth than did diopside in this series.

C. *Analysis of Data*

The preceding data may be explained qualitatively by considering the changes in viscosity and liquidus temperature with the changes in composition. It would be expected that a high viscosity would decrease the rate of growth by decreasing the mobility of the atoms, molecules, or groups which attach to the growing crystal. A lowered liquidus temperature in a given series of glasses should decrease the rate of growth by a lowering of the temperature of reaction and by a lowering of the amount of material available for crystal growth.

In the magnesia series, the temperature at which cristobalite and devitrite are in equilibrium with the melt is lowered with the addition of magnesia as is the viscosity.[10] It would be expected from the above discussion that the rate of crystal growth should belowered markedly with this combination, as was found to be the case.

In the case of a rising liquidus temperature and a rising viscosity, the factors tend to counteract each other and the effect on the maximum rate of crystal growth depends upon the magnitude of the changes. Thus when alumina is added to the soda-lime-silica glass, the liquidus of devitrite was progressively increased and the

viscosity was increased.[11] The rate of crystal growth decreased showing that the viscosity change had the greater influence.

In the case of wollastonite, the liquidus temperature increased again as the viscosity was increased.[11] However, in this case, the rate of crystal growth at first remained constant showing that a balance had been reached between the opposing factors. Further additions of alumina increased the rate, indicating that the high liquidus temperature had a dominating influence.

The changes in the maximum rate of growth of diopside were similar to the wollastonite changes. The viscosity of the glass and the liquidus temperature both increased while the rate of crystal growth increased slightly, indicating that the effect of the liquidus temperature change was dominant.

A consideration of changes in the rates of crystal growth in the various glasses with changes in the viscosity indicated that no simple relation is evident for the effect of viscosity on crystal growth since other factors must be considered.

IV. Other Experiments Relating to Crystal Growth

A. *Study of Surface Devitrification*

Since crystal growth almost invariably begins on the surface of glasses, an exploratory investigation was conducted in order that the phenomenon of surface devitrification could be more completely understood.

A specimen of glass was placed in a "Vycor" tube which was cleansed as much as possible. Air was filtered and drawn over the specimen using an aspirator. The sample was broken by thermal shock, the fresh surfaces were separated slightly by shaking the assembly, the tube was inserted in a furnace, and heated at 800°C. for twelve hours. A similar sample was given the same treatment except that the filter was omitted.

The sample which was in the atmosphere with reduced dust content showed very little devitrification on the fresh surface, while the sample which had been exposed to the ordinary atmospheric dust had very extensive devitrification on the fresh surface.

Since loss of alkali and adsorption of water vapor could occur with both samples, it was concluded that the dust in the air plays a dominant role in the promotion of surface devitrification.

B. *Study of Diffusion of Similar Glasses*

Since diffusion is of major importance to the growth of crystals in glasses, an exploratory investigation was conducted to determine possible methods for studying the inter-diffusion of similar-type glasses.

Two potash-lime-silica glasses were made which would not devitrify at 930°C., but would form such a composition, when inter-diffused, that a crystalline phase would precipitate. These glasses were heated in contact at 930°C. taking precautions to minimize the flow at the surface of contact. They were held at this temperature for 32 hours, removed from the furnace, sectioned, and the development of crystals was noted.

The interface showed a very thin zone of crystals, varying from 0.016 to 0.4 mm. It was assumed that the variations in thickness resulted from a slight flow of the glasses due to improper fitting of the specimens together.

The very thin zone of crystals may have been due to the slow rate of diffusion at the temperature studied or it may have been due to the action of the crystalline phase as a hindrance to further diffusion.

The method is capable of extension to measurements of diffusion of similar glasses at higher temperature. After exposing the glasses to high temperatures, the temperature can be lowered so that the crystalline phase of the mixed glass precipitates and the development of crystals thus indicates the extent of the inter-diffusion at the high temperature.

C. *Effect of Minor Addition on Rate of Crystal Growth*

It was the purpose of this phase of the investigation to make a preliminary survey of the effect of some minor constituents

commonly present in glasses on the rate of development of crystals in a glass.

A soda-lime-silica glass was prepared using the conventional batch containing carbonates. Other glasses were made with water, a small amount of sodium sulfate, sodium chloride, sodium carbonate, sodium fluoride, and arsenic trioxide in the batches. The theoretical sodium content was maintained constant in all cases. Pieces of each glass were placed on platinum foil and given the same heat treatment so that devitrification proceeded, after which they were sectioned and the thickness of the crystallized zone measured.

Water, sulfate, and fluoride increased the rate of growth of crystals while chloride and arsenic oxide decreased the rate. The changes may have been due to changes in the viscosity of the glass, to changes in the affinity for atoms, molecules, and groups on the growing crystal, or to other factors.

V. Summary

In this investigation it was shown that changes in the composition of a glass change the rate of crystal growth, the temperature of the maximum rate of crystal growth, and the nature of the crystalline phases precipitating. These changes were explained by considering the viscosity and liquidus temperature changes of the glasses, a low viscosity and a high liquidus temperature in a given series of glasses being associated with a high rate of crystal growth.

It was also shown that:

1. The linear growth of crystals in glasses proceeds at a practically constant rate until the crystallization zones of the glass meet.

2. The rate of growth vs. temperature curve is continuous through the liquidus temperature with the rate of solution vs. temperature curve, if solution is considered to be negative growth.

3. The rate of solution of crystals by the glass from which they were derived increases rapidly with an increase in temperature above the liquidus.

4. Alumina additions up to approximately seven percent decreased the maximum rate of crystal growth in a soda-lime-silica glass, while larger additions increased the rate.

5. The replacement of lime with magnesia up to approximately seven percent in a soda-lime-silica glass decreased the maximum rate of crystal growth; further replacement increased the rate of growth.

6. A sodium magnesium silicate, $Na_2O \cdot 2MgO \cdot 6SiO_2$, can occur as a devitrification product in high magnesia glasses.

7. No simple relation is evident for the effect of viscosity on the rate of crystal growth in glasses with variable magnesia or alumina content.

8. Dust and other material in the air play a major role in the promotion of surface devitrification.

9. Liquidus temperatures can be determined rapidly by measuring the rate of crystal growth and rate of crystal solution in a decreasing temperature interval.

10. Minor constituents commonly present in glasses may influence the rate of crystal growth considerably.

11. A method is presented by which the inter-diffusion of similar-type glasses may be followed.

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VITA

Howard Raymond Swift was born in Streator, Illinois, on March 3, 1920. He received his elementary education in the public schools of that city, graduating from Streator Township High School in June, 1936.

He entered the University of Illinois in the fall of 1936 and was graduated from that institution in June, 1940, with High Honors, with a B.S. degree in Ceramics. From June, 1940, until September 1, 1940, he worked in the laboratory of the General Electric Company at Cleveland, Ohio. From September 1, 1940, until July 1, 1942, he held a position as Research Assistant in Ceramic Engineering at the University of Illinois. At the same time, he enrolled in the Graduate School and received the degree of Master of Science in Ceramic Engineering in June, 1942. During the summer of 1941, he worked in the laboratory of the Chicago Vitreous Enamel Products Company, of Cicero, Illinois, and during the summer of 1942, he worked as a Special Research Appointee at the University of Illinois on a project sponsored by the Graduate

School. From September 1, 1942, until July 1, 1943, he held a Graduate School Fellowship at the University of Illinois. During the summer of 1943, he worked in the research laboratory of Anthony Company, Inc., at Streator, Illinois. From October 1, 1943, until October 1, 1944, he held a position as Special Research Associate in Ceramic Engineering at the University of Illinois, during which time he worked on "The Use of Strontium Compounds in Ceramics." From October 1, 1944, until the present time, he has held a Graduate School Fellowship at the University of Illinois.

The author is a member of Sigma Xi, Phi Kappa Phi, Keramos, Tau Beta Pi, Pi Mu Epsilon, and the American Ceramic Society.

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